Equation of State and Glass Transition of Stretched Network Polymers

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ABSTRACT: The glassy state and the glass transition of a stretched network polymers are studied on the basis of the hole theory introducing the concept of ordering parameters in non-equilibrium thermodynamics, where the hole and the conformation of network chain are supposed to be frozen-in in the glassy state. The equations for the change in glass transition temperature with stretching are derived to test the criteria for glass transition, *i.e.*, the iso-free volume, the iso-configurational entropy, and the iso-configurational energy assumptions. It was found that the second assumption explains the experimental facts best. The enthalpy and volume of the glass having histories of stretching are also evaluated. The difference in the enthalpy between stretched and non-stretched glasses depends not only on the change in the conformational energy with stretching but also on the differences in volume and glass-forming temperature.

KEY WORDS Polymer / Glassy State / Equation of State / Glass Transition / Stretch / Enthalpy /

In order to understand the glass transition and glassy state of amorphous polymers, the author has already investigated, on the basis of the hole theory, the pressure effects on the glass transition, and the thermodynamic behaviors of those glasses of different thermal and pressure histories.¹ It was concluded that the glass transition point is not the iso-free volume state, but near the iso-configurational entropy or energy state, and it was suggested that the chain flexibility also plays a role in the segmental motion as important as the free volume. In this paper, stretched network polymers are studied using the same treatment as in a previous paper.¹ The present study has two main aims; one is to derive the thermodynamic relations for the change in the glass transition temperature with stretching in order to test the criteria for the glass transition, and the other is to derive the expressions for the thermodynamic quantities of the glass having histories of stretching.

The treatment of the glass transition temperature and the glassy state adopted here is the same as that used in a previous paper,¹ and is described in general terms as follows.

First one defines the two kinds of parameters which determine the thermodynamic state of a system specified, for example, by the free energy

F ; one is not frozen and the other is frozen in the glassy state. Let us denote the former by $x_1, x_2, \dots, x_i, \dots, x_n$, and the latter by $y_1, y_2, \dots, y_i, \dots, y_m$. All of the former quantities are not generally independent. When the temperature T and volume V are taken as thermodynamic variables, x_i is supposed to be determined by giving the set of variables $(T, V, y_1, \dots, y_m)$. The latter one, y_i , corresponds to the ordering parameters or internal variables in the thermodynamic treatments of relaxation phenomena presented by Meixner and Davies—Jones *et al.*²

The total differential of Helmholtz free energy F is then written as

$$dF = \sum_{i=1}^n (\partial F / \partial x_i)_{x_{j \neq i}, y} dx_i + \sum_{i=1}^m (\partial F / \partial y_i)_{x, y_{j \neq i}} dy_i \quad (1)$$

$$= \sum_{i=1}^n (\partial F / \partial x_i)_{x_{j \neq i}, y} \{ (\partial x_i / \partial T)_{V, y} dT + (\partial x_i / \partial V)_{T, y} dV \} - \sum_{i=1}^m A_i dy_i \quad (1')$$

where A_i is the affinity for y_i defined by

$$A_i \equiv -(\partial F / \partial y_i)_{T, V, y_{j \neq i}} = -\{ (\partial F / \partial y_i)_{x, y_{j \neq i}} + \sum_{k=1}^n (\partial F / \partial x_k)_{x_{j \neq i}, y} (\partial x_k / \partial y_i)_{T, V, y_{j \neq i}} \} \quad (2)$$

In the liquid state, which is an equilibrium state, the affinity is zero;

$$A_i = 0. \quad (3)$$

On the other hand, in the glassy state,

$$y_i = y_{ig} = \text{constant} \quad (4)$$

or

$$dy_i = 0 \quad (5)$$

where y_{ig} is y_i at which the system is frozen-in, i.e., y_i at the glassforming point.

On the other hand, since the system is specified by the set of parameters $(x_1, \dots, x_n, y_1, \dots, y_m)$, the total differential of a thermodynamic quantity X is also expressed in general as

$$dX = \sum_{i=1}^n (\partial X / \partial x_i)_{x_{j \neq i}, y} dx_i + \sum_{i=1}^m (\partial X / \partial y_i)_{x, y_{j \neq i}} dy_i. \quad (6)$$

The conditions of eq 3 and 4 (or 5) lead to the thermodynamic quantities for the liquid and glassy states. For example, the equation of state for an unstretched substance is given from eq 1 or 1' by

$$P = -(\partial F / \partial V)_T = - \sum_{i=1}^n (\partial F / \partial x_i)_{x_{j \neq i}, y} (\partial x_i / \partial V)_{T, y} \quad (7)$$

with $A_i = 0$, for liquid state, and

$$P = - \sum (\partial F / \partial x_i)_{x_{j \neq i}, y=y_g} (\partial x_i / \partial V)_{T, y=y_g} \quad (8)$$

with $y_i = y_{ig}$, for the glassy state, where P is pressure. The difference in the change of thermodynamic quantity X between the liquid and glassy states is expressed from eq 6 with eq 3 and 5 as

$$\begin{aligned} \Delta(dX) &\equiv (dX)^l - (dX)^g = (dX)_{A=0} - (dX)_y \\ &= \sum_{i=1}^n (\partial X / \partial x_i)_{x_{j \neq i}, y} \Delta(dx_i) \\ &\quad + \sum_{i=1}^m (\partial X / \partial y_i)_{x, y_{j \neq i}} (dy_i)_{A=0} \quad (9)^* \end{aligned}$$

Here, the symbol Δ designates the difference between the liquid and glassy states, the superscripts l and g represent the quantities in the liquid and glassy states, respectively, and the subscripts $A=0$ and y indicate the fixed variables in the differentials.

In the previous treatments, another assumption was introduced in order to define the configurational part of a thermodynamic quantity, entropy or internal energy, which is frozen in the glassy

state, as a function of state. Namely, the free energy of a system was assumed to be formally expressed as

$$F = U^c(y_1, y_2, \dots, y_m) - TS^c(y_1, y_2, \dots, y_m) + U^*(x_1, x_2, \dots, x_n) - TS^*(x_1, x_2, \dots, x_n) \quad (10)$$

where U^c is the configurational energy, and S^c the configurational entropy. This assumption for the form of F was required in order to define S^c (or U^c) as a part of S (or U) which is frozen-in in the glassy state and is determined by y only. The frozen parameters y specify the configuration of chain molecules in the system. Unless the part of the entropy related to the configuration can be separately evaluated (as in eq 10) at least approximately, "the configurational entropy" will lose its meaning. It was deduced from this assumption, as indicated previously in the hole model,¹ that the thermal expansion coefficient α , compressibility β and heat capacity C_p of a glass are almost independent of the frozen parameters which are determined by the condition of the glass formation. If there exists a term of S (and/or U) which depends strongly both on x and y and can not be expressed separately as the form of eq 10, such quantities as α , β and C_p of a glass should depend strongly on y , i.e., on the history of the glass. The assumption of eq 10, therefore, also implies that α , β , and C_p are almost independent of the history of the glass, in accordance with experiments. This is also supported by the fact that the excess entropy of the glassy state relative to the crystalline state is almost independent of temperature. Since the crystalline state

* When X is regarded as a function of $(T, P, y_1, \dots, y_m)$, one has an alternative form equivalent to eq 9 using eq 3, 5, and 6;

$$\Delta(dX) = \sum_{i=1}^m (\partial X / \partial y_i)_{T, P} (dy_i)_{A=0}$$

which is reformed as

$$\begin{aligned} \Delta(dX) &= \sum_{i=1}^m \left\{ \sum_{k=1}^n (\partial X / \partial x_k)_{x_{j \neq k}, y} (\partial x_k / \partial y_i)_{T, P} \right. \\ &\quad \left. + (\partial X / \partial y_i)_{x, y_{j \neq i}} \right\} (dy_i)_{A=0} \\ &= \sum_{k=1}^n (\partial X / \partial x_k)_{x_{j \neq k}, y} \sum_{i=1}^m (\partial x_k / \partial y_i)_{T, P} (dy_i)_{A=0} \\ &\quad + \sum_{i=1}^m (\partial X / \partial y_i)_{x, y_{j \neq i}} (dy_i)_{A=0} \\ &= \text{the right hand side of eq 9} \end{aligned}$$

can be regarded as a kind of frozen state. The conventional way to evaluate the configurational entropy S^c , i.e., the estimation of S^c by the equation

$$S^c(T) = S^c(T_0) + \int_{T_0}^T (\Delta C_p / T) dT,$$

where ΔC_p is the difference in C_p between the liquid and crystalline states, is essentially based on the assumption of eq 10 with $\Delta(dx_i/dT) = 0$ as seen in eq 12 described below. Under the assumption of eq 10, $(dZ^c)^1 (Z=S \text{ or } U)$ can be written as

$$(dZ^c)^1 = \sum_{i=1}^m (\partial Z / \partial y_i)_{x, y_{j \neq i}} (dy_i)_{A=0} \quad (11)$$

Therefore, from eq 9 the change in the configurational quantity $(dZ^c)^1$ is expressed as

$$(dZ^c)^1 = \Delta(dZ) - \sum_{i=1}^n (\partial Z / \partial x_i)_{x_{j \neq i}, y} \Delta(dx_i) \quad (12)$$

Generally speaking, $\Delta(dx_i)$ is not zero, and it must be noticed therefore that the change in the configurational part of the thermodynamic quantity is not always expressed as the difference in the change in the thermodynamic quantity between the liquid and glassy states.

The change of X_s with Y_t at the glass transition point, $(\partial Y_s / \partial Y_t)_g$, is expressed in terms of $(\partial X / \partial Y_t)_g$, or $(\partial X / \partial Y_s)_g$, as

$$\begin{aligned} (\partial Y_s / \partial Y_t)_g &= \{ -(\partial X / \partial Y_t)_{Y_i \neq t} + (\partial X / \partial Y_t)_g \} / (\partial X / \partial Y_s)_{Y_i \neq s} \quad (13) \\ &= -(\partial X / \partial Y_t)_{Y_i \neq t} / \{ (\partial X / \partial Y_s)_{Y_i \neq s} - (\partial X / \partial Y_s)_g \} \quad (13') \end{aligned}$$

when the thermodynamical variables other than Y_s and Y_t are fixed.

In the preceding paper,¹ to deal with the change of the glass transition temperature with pressure, a hole model was adopted and the variables chosen as

$$x_i : V^*, T, \quad y_i : \tilde{V}, S_1^c, \quad Y : Y_s = T, Y_t = P$$

where V^* is the volume of the cells occupied with segments, $\tilde{V}$ is defined as V/V^* , and S_1^c is the conformational entropy of polymer chains. Since it is derived from eq 10 that $(\partial V^* / \partial T)_p$ and $(\partial V^* / \partial P)_T$ are continuous at the glass transition temperature,¹ it follows from eq 12 with $Z=S$ that

$$(\partial S^c / \partial T)_p^1 = \Delta(\partial S / \partial T)_p = \Delta C_p / T \quad (14)$$

and

$$(\partial S^c / \partial P)_T^1 = \Delta(\partial S / \partial P)_T = -V \Delta \alpha \quad (15)$$

where C_p is heat capacity under constant pressure $T(\partial S / \partial T)_p$, and α thermal expansion coefficient $(\partial \ln V / \partial T)_p$. Then, substituting eq 14 and 15 into eq 13 with $X=S^c$, one has

$$(\partial T / \partial P)_g = \{ TV \Delta \alpha + T(\partial S^c / \partial P)_g \} / \Delta C_p \quad (16)$$

This is one of the equations for $(\partial T / \partial P)_g$ obtained in a previous paper.¹ If the iso- S^c at the glass transition point is a valid assumption, i.e., $(\partial S^c / \partial P)_g = 0$, the relation $(\partial T / \partial P)_g = TV \Delta \alpha / \Delta C_p$ is derived from eq 16.

THEORETICAL

Model

A rectangular network polymer, consisting of N segments, of volume $V = \prod_{i=1}^3 L_i$ is considered, where L_i is the length in the i -th direction, and 1-direction ($i=1$) is taken as the direction of stretching. In the system, where M lattice sites are involved, there remain $(M-N)$ empty sites or holes. If the cell volume is denoted by v^* , $V \equiv M v^*$, and V^* is defined as $V^* \equiv N v^*$. Then, $\tilde{V} \equiv V / V^* = M / N$, and $(1 - \tilde{V}^{-1})$ represents the hole fraction. The cell dimensions are not necessarily isotropic and can be assumed to be expressed by $v^* = \prod_{i=1}^3 l_i^*$, where l_i^* is the representative length in the i -th direction of the cell. The quantity m_i is then defined as $L_i = m_i l_i^*$, and thus $M = \prod_{i=1}^3 m_i$. The occupied volume $V_0 = N v_0$ is assumed to be a constant independent of temperature, external pressure, and deformation. As the quantity which expresses the expansion of the cell volume, V^+ is defined by $V^+ \equiv V^* / V_0 = \prod_{i=1}^3 l_i^* / v_0^{1/3}$. Summing up the relations among the quantities defined above;

$$V = \prod_{i=1}^3 L_i \quad (17)$$

$$V^* = N v^* = N \prod_{i=1}^3 l_i^* \quad (18)$$

$$V^+ = V^* / V_0 = v^* / v_0 = \prod_{i=1}^3 l_i^+ \quad (19)$$

$$l_i^+ = l_i^* / v_0^{1/3} \quad (20)$$

$$\tilde{V} = V/V^* = M/N = \prod_{i=1}^3 m_i/N \quad (21)$$

$$L_i = m_i l_i^* \quad (22)$$

The total differential forms are;

$$\begin{aligned} d \ln V &= \sum_{i=1}^3 d \ln m_i + \sum_{i=1}^3 d \ln l_i^* \\ &= d \ln \tilde{V} + \sum_{i=1}^3 d \ln l_i^+ \end{aligned} \quad (23)$$

$$d \ln L_i = d \ln m_i + d \ln l_i^* \quad (24)$$

$$d \ln \tilde{V} = \sum_{i=1}^3 d \ln m_i \quad (25)$$

$$d \ln l_i^+ = d \ln l_i^* \quad (26)$$

$$d \ln V^+ = \sum_{i=1}^3 d \ln l_i^+ = \sum_{i=1}^3 d \ln l_i^* \quad (27)$$

In general, a distribution function for mean end-to-end vectors of network chains must be defined in order to specify the state of the chain conformations. The affine deformation is, however, assumed here, *i.e.*, it is assumed that the mean crosslinking point—to—crosslinking point vector ϵ for any chain is expressed in term of the displacement tensor γ as

$$\epsilon = \gamma \cdot \epsilon^* = \gamma' \cdot \epsilon_0 = b a \cdot \lambda \cdot \epsilon_{00} \quad (28)$$

$$\gamma' = a \cdot \lambda \quad (29)$$

$$\epsilon_0 = b \cdot \epsilon_{00} \quad (30)$$

where ϵ^* is ϵ in the unstretched state, ϵ_0 is ϵ when the chain is an uncrosslinked free chain at the same temperature and ϵ_{00} is ϵ_0 at the temperature of crosslinking. a is associated with the change in ϵ arising from variations of bond length and small deviations of rotational angles from stable positions (*e.g.*, *trans* and *gauche*), being variable both in the glassy and liquid states, and λ and b are associated with the change in ϵ caused by the variation of *trans-gauche* conformations, which are frozen-in in the glassy state. The former, λ , is related to stretching and the latter scalar quantity b is a function of temperature alone, representing the change in the unperturbed chain dimension with temperature. In the present paper, only simple elongation is considered. Then, a and λ are written as

$$a = \begin{pmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{pmatrix}, \quad \lambda = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \quad (31)$$

Therefore, from eq 28 and 31, one has

$$d \ln L_i = d \ln \lambda_i + d \ln a_i + d \ln b \quad (32)$$

The glassy state is dealt with here as a quasi-equilibrium state, *i.e.*, it is regarded as a frozen liquid such that polymer chains cannot change their *trans-gauche* conformations and cannot exchange their mean positions with each other. Thus, in the glassy state, the lattice number and arrangement specified by m_i , accordingly the hole fraction specified by $\tilde{V}$ (eq 21), and the state of chain conformations specified by λ and b are assumed to be completely frozen-in. Namely, the quantities m_i , $\tilde{V}$, λ , and b are constant in the glassy state, and correspond to internal variables y described in the introduction. Since m_1 , m_2 , m_3 , and $\tilde{V}$ are related with each other by eq 25, three of them are independent variables in general and can be chosen as y . On the other hand, a_i and l_i^+ are variable both in the liquid and glassy states, and correspond to the nonfrozen parameters x .

The free energy of the system is assumed here to be expressed by the sum of two kinds of free energy; one associated with the internal degrees of freedom or intrasegmental interactions including the interactions related to the chain conformations, and the other associated with the external degrees of freedom or intersegmental interactions. The former is considered to be independent of volume and depends on the state of chain conformations and temperature. Hence it can be regarded as a function of λ , a , b and T . On the other hand, the latter (free energy) should depend upon the hole fraction, the mean distance between nearest neighbor segments (the cell dimension) and temperature. Therefore, it can be regarded as a function of $\tilde{V}$, l_i^+ , and T . The free energy may not directly depend on m_i but on $\tilde{V}$. Such an assumption, that the two kinds of free energy related respectively to chain conformations and liquidlike properties are expressed separately, was adopted in a previous paper¹ and was also introduced in the statistical theory of rubber elasticity.³

The form of eq 10 is now introduced also in the present theory. Then, under the above as-

sumption the free energy of the system is expressed in the form;

$$\begin{aligned} F &= F_1(\lambda, b, a, T) + F_2(\tilde{V}, l_{1,2,3}^+, T) \\ &= U_1^c(\lambda, b) - TS_1^c(\lambda, b) + U_1^a(a, T) - TS_1^a(a, T) \\ &\quad + U_2^c(\tilde{V}) - TS_2^c(\tilde{V}) + U_2^+(l_{1,2,3}^+, T) \\ &\quad - TS_2^+(l_{1,2,3}^+, T) \end{aligned} \quad (33)$$

where the subscripts 1 and 2 refer to intra- and inter-segmental interactions, respectively.

Equation of State

The equation of state for simple elongation can be derived in the conventional manner:

$$V(\sigma - P) = (\partial F / \partial \ln L_1)_{T, L_{2,3}} \quad (34)$$

$$-VP = (\partial F / \partial \ln L_2)_{T, L_{3,1}} \quad (35)$$

where σ is the tensile stress, the tensile force per unit area. In the case of simple elongation, since the total differential of F is written, corresponding

to eq 1', as $dF = -S dT - P d\tilde{V} + f dL_1 - \sum_{i=1}^m A_i dy_i$

(f , tensile force), the affinity A_i is defined as $A_i = -(\partial F / \partial y_i)_{T, V, L_1, y_{j \neq i}}$ with $L_2 = L_3$, where $y = \{\lambda_1, \lambda_2, \lambda_3, m_1, m_2, m_3, b\}$. Then, in the liquid state, the equilibrium conditions, $A_i = 0$, are satisfied, which are written, with the aid of eq 23–26, 32 and 33, as

$$\begin{aligned} A_{\lambda_i} &\equiv -(\partial F / \partial \lambda_i)_{T, V, L_1, \lambda_{j \neq i}, m_{1,2,3}, b} \\ &= -(\partial F / \partial \lambda_i)_{\tilde{V}, l_{1,2,3}^+, \lambda_{j \neq i}, a_{j \neq i}, b, T} \\ &= 0 \end{aligned}$$

$$\begin{aligned} A_{m_i} &\equiv -(\partial F / \partial m_i)_{T, V, L_1, \lambda, m_{j \neq i}, b} \\ &= -(\tilde{V} / m_i) (\partial F / \partial \tilde{V})_{l_{1,2,3}^+, \lambda, a, b, T} \\ &= (l_i^+ / m_i) (\partial F / \partial l_i^+)_{l_{j \neq i}^+, \lambda, a, b, T} \\ &= 0 \end{aligned} \quad (36)$$

Using the relations of eq 23–27 and eq 32, eq 36 yields

$$K_1^+ = K_2^+ = K_3^+ = \tilde{K} \quad (37)$$

$$K_1^\lambda = K_1^a, \quad K_2^\lambda = K_2^a = K_3^\lambda = K_3^a \quad (38)$$

where

$$K_i^+ = (\partial F / \partial \ln l_i^+)_{\tilde{V}, \lambda, l_{j \neq i}^+, a, b, T} \quad (39)$$

$$\tilde{K} = (\partial F / \partial \ln \tilde{V})_{l_{1,2,3}^+, \lambda, a, b, T} \quad (40)$$

$$K_i^\lambda = (\partial F / \partial \ln \lambda_i)_{\tilde{V}, l_{1,2,3}^+, \lambda_{j \neq i}, a, b, T} \quad (41)$$

$$K_i^a = (\partial F / \partial \ln a_i)_{\tilde{V}, l_{1,2,3}^+, \lambda, a_{j \neq i}, b, T} \quad (42)$$

The eq 37 gives

$$l_1^+ = l_2^+ = l_3^+ \quad (43)$$

which indicates that the liquidlike properties are isotropic in the liquid state in the present treatment. The equation of state in the liquid state is then expressed, from eq 34, 35, 37, and 38, as

$$V(\sigma - P) = K_1^\lambda + K_1^+ \quad (44)$$

$$-VP = K_2^\lambda + K_2^+ \quad (45)$$

with $K_i^\lambda = K_i^a$ and $K_1^+ = K_2^+ = K_3^+ = \tilde{K}$. From eq 44 and 45, the tensile force $f = \sigma V / L_1$ is

$$f = (K_1^\lambda - K_2^\lambda) / L_1 \quad (46)$$

On the other hand, in the glassy state λ_i , $\tilde{V}$, m_i , and b are kept constant, then it follows, from eq 23–27, 32, 34, and 35 with $d \ln \lambda_i = d \ln \tilde{V} = d \ln m_i = d \ln b = 0$, that

$$V(\sigma - P) = K_1^a + K_1^+ \quad (47)$$

$$-VP = K_2^a + K_2^+ \quad (48)$$

$$f = \{(K_1^a - K_2^a) + (K_1^+ - K_2^+)\} / L_1 \quad (49)$$

At the glass transition point, $K_1^+ = K_2^+$, $K_i^\lambda = K_i^a$, and therefore it is seen from eq 46 and 49 that f is continuous at the transition.

From the equation of state one can now evaluate the thermal expansion coefficient, compressibility, Poisson's ratio, and Young's modulus, which will be defined in the following, in terms of the derivatives of free energy and entropy with respect to the parameters involved in the theory:

thermal expansion coefficient;

$$\alpha_{1L} = (\partial \ln V / \partial T)_{P, L_1}^1 \quad (50)$$

$$\alpha_{1L}^+ = (\partial \ln V^+ / \partial T)_{P, L_1}^1 \quad (51)$$

$$\alpha_{gL} = (\partial \ln V / \partial T)_{P, L_1}^g \quad (52)$$

$$\alpha_g = (\partial \ln V / \partial T)_{P, \sigma=0}^g \quad (53)$$

isothermal compressibility

$$\beta_{1L} = -(\partial \ln V / \partial P)_{T, L_1}^1 \quad (54)$$

$$\beta_{1L}^+ = -(\partial \ln V^+ / \partial P)_{T, L_1}^1 \quad (55)$$

$$\beta_{gL} = -(\partial \ln V / \partial P)_{T, L_1}^g \quad (56)$$

$$\beta_g = -(\partial \ln V / \partial P)_{T, \sigma=0}^g \quad (57)$$

Poisson's ratio

$$\mu_1 = -(\partial \ln L_2 / \partial \ln L_1)_{P, T}^1 \quad (58)$$

$$\mu_g = -(\partial \ln L_2 / \partial \ln L_1)_{P, T}^g \quad (59)$$

Young's modulus

$$E_1 = (\partial \sigma / \partial \ln L_1)_{P, T}^1 \quad (60)$$

$$E_g = (\partial \sigma / \partial \ln L_1)_{P,T}^g \quad (61)$$

The superscripts l and g again indicate the derivatives in the liquid and glassy states respectively. The following derivatives are also defined here:

$$K_{ij}^+ = (\partial K_i^+ / \partial \ln l_j^+) \tilde{V}, l_{k \neq j}^+, T \quad (62)$$

$$\tilde{K} = (\partial \tilde{K} / \partial \ln \tilde{V})_{l_{1,2,3}^+, T} \quad (63)$$

$$K_{ij}^\lambda = (\partial K_i^\lambda / \partial \ln \lambda_j) \lambda_{k \neq j}, b, a, T \quad (64)$$

$$K_{ij}^a = (\partial K_i^a / \partial \ln a_j) \lambda, b, a_{k \neq j}, T \quad (65)$$

As the results, from eq 44, 45, 47, and 48 with eq 37 and 38 for the liquid state, the following expressions are obtained (The derivations are shown in APPENDIX I).

$$\alpha_{1L} - \alpha_{1L}^+ = \{(\partial S_2^c / \partial \ln \tilde{V}) - (\partial K_2^\lambda / \partial T)_{P,L_1}^1 - VP\alpha_{1L}\} / \tilde{K} \quad (66)$$

$$\alpha_{1L}^+ = -3\{(\partial K_2^+ / \partial T)_{l_{1,2,3}^+, T} + (\partial K_2^\lambda / \partial T)_{P,L_1}^1 + PV\alpha_{1L}\} / \sum_{k=1}^3 K_{2k}^+ \quad (67)$$

$$\alpha_{gL} = -\{(\partial K_2^+ / \partial T)_{l_{1,2,3}^+, T} + (\partial K_2^a / \partial T)_{a_{1,2,3}}\} / \{ \sum_{k=2}^3 K_{2k}^+ / 2 + \sum_{k=2}^3 K_{2k}^a / 2 + PV \} \quad (68)$$

$$\alpha_g = -\{(\partial K_2^+ / \partial T)_{l_{1,2,3}^+, T} + (\partial K_2^a / \partial T)_{a_{1,2,3}}\} / \{ \sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+ / \partial \ln V)_{P,\sigma=0}^g + \sum_{k=1}^3 K_{2k}^a (\partial \ln a_k / \partial \ln V)_{P,\sigma=0}^g + PV \} \quad (69)$$

$$\beta_{1L} - \beta_{1L}^+ = V\{1 - (P + P^\lambda)\beta_{1L}\} / \tilde{K} \quad (70)$$

$$\beta_{1L}^+ = 3V\{1 - (P + P^\lambda)\beta_{1L}\} / \sum_{k=1}^3 K_{2k}^+ \quad (71)$$

$$\beta_{gL} = (P + P^a + \sum_{k=2}^3 K_{2k}^+ / 2V)^{-1} \quad (72)$$

$$\beta_g = \{P + P^a + \sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+ / \partial V)_{T,\sigma=0}^g\}^{-1} \quad (73)$$

$$1 - 2\mu_1 = (\partial \ln V / \partial \ln L_1)_{T,P}^1 = \frac{(\partial K_2^\lambda / \partial \ln L_1)_{T,P}^1 (3\tilde{K} + \sum_{k=1}^3 K_{2k}^+)}{\tilde{K} \sum_{k=1}^3 K_{2k}^+ + PV(3\tilde{K} + \sum_{k=1}^3 K_{2k}^+)} \quad (74)$$

$$1 - 2\mu_g = (\partial \ln V / \partial \ln L_1)_{T,P}^g = 1 - (K_{21}^a + K_{21}^+ + PV) / (\sum_{k=2}^3 K_{2k}^+ / 2 + P^a V + PV) \quad (75)$$

$$E_g = \{K_{11}^a + K_{11}^+ - 2(K_{12}^a + K_{12}^+) \mu_g\} / V - (1 - 2\mu_g)(\sigma - P) \quad (76)$$

$$\sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+ / \partial L_1)_{T,L}^1 = \tilde{K} (\partial \ln V / \partial L_1)_{T,P}^1 \quad (77)$$

where

$$P^\lambda = \sum_{k=1}^3 K_{2k}^\lambda (\partial \ln \lambda_k / \partial V)_{T,L_1}^1 \quad (78)$$

$$P^a = \sum_{k=1}^3 K_{2k}^a (\partial \ln a_k / \partial V)_{T,L_1}^g = \sum_{k=2}^3 K_{2k}^a / 2V \quad (79)$$

$$P_0^a = \sum_{k=1}^3 K_{2k}^a (\partial \ln a_k / \partial V)_{T,\sigma=0}^g \quad (80)$$

On the other hand, heat capacity is evaluated as follows.

Heat capacity under constant pressure C_p consists of two parts because of the form of free energy eq 33:

$$C_p = C_p^{\text{inter}} + C_p^{\text{intra}} \quad (81)$$

where the superscripts inter and intra refer to inter- and intra-segmental interactions. From the definition of C_p and eq 23, one has

$$\begin{aligned} C_{p1L}^{\text{intra}} &= T(\partial S_1 / \partial T)_{P,L_1}^1 \\ &= T(\partial S_1^c / \partial T)_{P,L_1} + T(\partial S_1^a / \partial T)_{P,L_1} \\ &= \sum_{k=1}^3 T(\partial S_1^c / \partial \ln \lambda_k)_b (\partial \ln \lambda_k / \partial T)_{P,L_1}^1 \\ &\quad + T(\partial S_1^c / \partial T)_{\lambda_{1,2,3}} + \sum_{k=1}^3 T(\partial S_1^a / \partial \ln a_k)_T \\ &\quad \times (\partial \ln a_k / \partial T)_{P,L_1}^1 + T(\partial S_1^a / \partial T)_{a_{1,2,3}} \end{aligned} \quad (82)$$

where it was noticed that b is a function of T alone. Similarly,*

* The heat transferred to the material in an infinitesimal process, δQ , is expressed as²

$$\delta Q = TdS - \sum_i A_i dy_i$$

In the liquid state, an equilibrium state, $A_i = 0$, therefore, one has $\delta Q = TdS$. On the other hand, in the glassy state, $dy_i = 0$ is assumed here, accordingly $\delta Q = TdS$ also holds. Hence, the heat capacity is evaluated as $T(dS/dT)$ even in the glassy state where $A_i \neq 0$. Only in an irreversible process where the change of y_i occurs in a non-equilibrium state ($dy_i \neq 0$ and $A_i \neq 0$), one has $\delta Q \neq TdS$ and $TdS - \delta Q = \sum_i A_i dy_i > 0$, when thermal and pressure equilibria are assumed as is done in this paper.

$$\begin{aligned}
C_{pgL}^{\text{intra}} &\equiv T(\partial S_1/\partial T)_{p,L_1}^g = T(\partial S_1^a/\partial T)_{p,L_1}^g \\
&= T \sum_{k=1}^3 (\partial S_1^a/\partial \ln a_k)_T (\partial \ln a_k/\partial T)_{p,L_1}^g \\
&\quad + T(\partial S_1^a/\partial T)_{a_{1,2,3}} \\
&= T\alpha_{gL} \sum_{k=2}^3 (\partial S_1^a/\partial \ln a_k)_T/2 + T(\partial S_1^a/\partial T)_{a_{1,2,3}}
\end{aligned} \quad (83)$$

In the derivation of eq 84 from eq 83, $(\partial \ln a_1/\partial T)_{p,L_1}^g = 0$ and $(\partial \ln a_2/\partial T)_{p,L_1}^g = (\partial \ln a_3/\partial T)_{p,L_1}^g = \alpha_{gL}$ were used. On the other hand, one may derive from the form of expression for S in eq 33

$$\begin{aligned}
C_{pg}^{\text{intra}} &\equiv T(\partial S_1/\partial T)_{p,\sigma=0}^g = T(\partial S_1^a/\partial T)_{p,\sigma=0}^g \\
&= T \sum_{k=1}^3 (\partial S_1^a/\partial \ln a_k)_T (\partial \ln a_k/\partial T)_{p,\sigma=0}^g \\
&\quad + T(\partial S_1^a/\partial T)_{a_{1,2,3}}
\end{aligned} \quad (84)$$

Heat capacity C_p^{inter} associated with intersegmental interactions is also derived as follows in the same way as the above:

$$\begin{aligned}
C_{p1L}^{\text{inter}} &= T(\partial S_2^c/\partial \ln \tilde{V})(\partial \ln \tilde{V}/\partial T)_{p,L_1}^1 \\
&\quad + T \sum_{k=1}^3 (\partial S_2^+/ \partial \ln l_k^+)_{T,l_i^+ \neq k} \\
&\quad \times (\partial \ln l_k^+/\partial T)_{p,L_1}^1 + T(\partial S_2^+/\partial T)_{l_{1,2,3}}^+ \\
&= T(\alpha_{1L} - \alpha_{1L}^+) (\partial S_2^c/\partial \ln \tilde{V}) \\
&\quad + T\alpha_{1L} \sum_{k=1}^3 (\partial S_2^+/\partial \ln l_k^+)_{T,l_i^+ \neq k}/3 \\
&\quad + T(\partial S_2^+/\partial T)_{l_{1,2,3}}^+
\end{aligned} \quad (85)$$

$$\begin{aligned}
C_{p1L}^+ &\equiv T(\partial S_2^+/\partial T)_{p,L_1}^1 \\
&= T\alpha_{1L} \sum_{k=1}^3 (\partial S_2^+/\partial \ln l_k^+)_{T,l_i^+ \neq k}/3 \\
&\quad + T(\partial S_2^+/\partial T)_{l_{1,2,3}}^+
\end{aligned} \quad (86)$$

$$C_{p1L}^{\text{inter}} - C_{p1L}^+ = T(\alpha_{1L} - \alpha_{1L}^+) (\partial S_2^c/\partial \ln \tilde{V}) \quad (87)$$

$$\begin{aligned}
C_{gL}^{\text{inter}} &= T \sum_{k=1}^3 (\partial S_2^+/\partial \ln l_k^+)_{T,l_i^+ \neq k} (\partial \ln l_k^+/\partial T)_{p,L_1}^g \\
&\quad + T(\partial S_2^+/\partial T)_{l_{1,2,3}}^+ \\
&= T\alpha_{gL} \sum_{k=2}^3 (\partial S_2^+/\partial \ln l_k^+)_{T,l_i^+ \neq k}/2 \\
&\quad + T(\partial S_2^+/\partial T)_{l_{1,2,3}}^+
\end{aligned} \quad (88)$$

$$\begin{aligned}
C_{pg}^{\text{inter}} &= T \sum_{k=1}^3 (\partial S_2^+/\partial \ln l_k^+)_{T,l_i^+ \neq k} \\
&\quad \times (\partial \ln l_k^+/\partial T)_{p,\sigma=0}^g + T(\partial S_2^+/\partial T)_{l_{1,2,3}}^+
\end{aligned} \quad (89)$$

Approximate Expressions

Further considerations will be made under those approximations which are reasonable as follows.

From the condition of equilibrium, eq 38, one obtains

$$\begin{aligned}
&(\partial U_1^a/\partial \ln a_i)_{a_j \neq i, T} - T(\partial S_1^a/\partial \ln a_i)_{a_j \neq i, T} \\
&= (\partial U_1^c/\partial \ln \lambda_i)_{\lambda_j \neq i, T} - T(\partial S_1^c/\partial \ln \lambda_i)_{\lambda_j \neq i, T} \\
&= K_i^\lambda
\end{aligned} \quad (90)$$

The first part of the left hand side of this equation indicates the stress, arising from the variation of bond length and small deviation of rotational angles from the stable positions, which may be considered to be almost the energetic force, i.e., $(\partial U_1^a/\partial \ln a_i)_{a_j \neq i, T} \gg T(\partial S_1^a/\partial \ln a_i)_{a_j \neq i, T}$. On the other hand, $T(\partial S_1^c/\partial \ln \lambda_i)_{\lambda_j \neq i, T}$ is a dominant part in K_i^λ (or the same order as K_i^λ), where K_i^λ designates the stress arising from the change in *trans-gauche* conformation. Therefore, it is assumed here that

$$T(\partial S_1^c/\partial \ln \lambda_i)_{\lambda_j \neq i, T} \gg T(\partial S_1^a/\partial \ln a_i)_{a_j \neq i, T} \quad (91)$$

or

$$(\partial K_i^\lambda/\partial T)_{\lambda_{1,2,3}} \gg (\partial K_i^a/\partial T)_{a_{1,2,3}} \quad (92')$$

On the other hand, eq 38 yields

$$\sum_{k=1}^3 K_{ik}^a (d \ln a_k)_T^1 = \sum_{k=1}^3 K_{ik}^\lambda (d \ln \lambda_k)_T^1 \quad (93)$$

Accordingly, it may be considered that

$$\begin{aligned}
&(\partial \ln a_k/\partial \ln L_1)_{T,P}^1 / (\partial \ln \lambda_i/\partial \ln L_1)_{T,P}^1 \\
&= O(K_{ik}^\lambda/K_{ik}^a) \ll 1
\end{aligned} \quad (94)$$

because the modulus K_{ik}^a for the stress K_i^a may be much larger than K_{ik}^λ , than for the stress K_i^λ .

In the present treatment the stretching of the network polymer in the liquid state under atmospheric pressure is considered, excluding the stretching in the glassy state with the stress larger than that of the stretching in the liquid state. The following conditions may then be satisfied, because P and σ are much smaller than the internal pressure P_i [$\equiv (\partial U/\partial V)_T \equiv T\alpha/\beta - P$] and the bulk modulus (β^{-1}) [$P_i = O(10^3 \text{ atm})$, $\beta^{-1} = O(10^5 \text{ atm})$], as seen from eq 66, 67, 70, 71, and 72 with $P_i \cong T(\alpha/\beta)$ and eq 94

$$P, P^2, \sigma \ll P^a, P_0^a \ll O(\beta^{-1}) = \tilde{K}, K_{ik}^+ \quad (95)$$

$$\begin{aligned}
T(\partial K_i^\lambda/\partial T)_{p,L_1}^1 &= O(\sigma) \ll O(P_i) \\
&= T(\partial S_2^c/\partial \ln \tilde{V}), T(\partial K_i^+/\partial T)_{l_{1,2,3}}^+
\end{aligned} \quad (96)$$

In the case considered here, the anisotropy in

the liquid-like properties is very small and may be ignored even in the glassy state; that is,

$$(\partial \ln I_k^+ / \partial \ln V)_{T, \sigma=0}^g = 1/3 \quad \text{for } k=1, 2, 3 \quad (97)$$

$$(\partial \ln I_k^+ / \partial T)_{p, \sigma=0}^g = \alpha_g / 3 \quad \text{for } k=1, 2, 3 \quad (98)$$

$$K_{ii}^+ = K_{jj}^+, \quad K_{12}^+ = K_{21}^+ = K_{23}^+ = K_{32}^+ = K_{31}^+ = K_{13}^+ \quad (99)$$

Then, one has from eq 70 and 71 with the aid of eq 95,

$$\beta_{1L} - \beta_{1L}^+ = V / \tilde{K} \quad (100)$$

$$\beta_{1L}^+ = 3V / \sum_{k=1}^3 K_{2k}^+ \quad (101)$$

On the other hand, eq 72 and 73 are expressed from eq 95 and 97 as

$$\beta_{gL} = 2V / \sum_{k=2}^3 (K_{2k}^+ + K_{2k}^a) \cong 2V / \sum_{k=2}^3 K_{2k}^+ \quad (102)$$

$$\beta_g = 3V / \sum_{k=1}^3 (K_{2k}^+ + K_{2k}^a) \cong 3V / \sum_{k=1}^3 K_{2k}^+ \quad (103)$$

With the use of eq 95, eq 66 and 67 reduce to

$$\alpha_{1L} - \alpha_{1L}^+ = (\partial S_2^c / \partial \ln \tilde{V}) / \tilde{K} \quad (104)$$

$$\alpha_{1L}^+ = -3(\partial K_2^+ / \partial T)_{i1,2,3} / (\sum_{k=1}^3 K_{2k}^+) \quad (105)$$

Under the condition of eq 92', 95, and 97, eq 68 and 69 yield

$$\alpha_{gL} = -2[(\partial K_2^+ / \partial T)_{i1,2,3} + (\partial K_2^a / \partial T)_{a1,2,3}] / \sum_{k=2}^3 (K_{2k}^+ + K_{2k}^a) \quad (106)$$

$$\cong -2(\partial K_2^+ / \partial T)_{i1,2,3} / \sum_{k=2}^3 K_{2k}^+ \quad (106')$$

$$\alpha_g = -3[(\partial K_2^+ / \partial T)_{i1,2,3} + (\partial K_2^a / \partial T)_{a1,2,3}] / \sum_{k=1}^3 (K_{2k}^+ + K_{2k}^a) \quad (107)$$

$$= -3(\partial K_2^+ / \partial T)_{i1,2,3} / \sum_{k=1}^3 K_{2k}^+ \quad (107')$$

Furthermore the approximation of eq 95 makes eq 74 reduce to

$$(\partial \ln V / \partial \ln L_1)_{T,P}^1 = -(\partial K_2^+ / \partial \ln L_1)_{T,P}^1 / \{3 / \sum_{k=1}^3 K_{2k}^+ + \tilde{K}^{-1}\} \quad (108)$$

and makes eq 75 deduce to

$$(\partial \ln V / \partial \ln L_1)_{T,P}^g = 1 - (2K_{21}^+ / \sum_{k=2}^3 K_{2k}^+) \quad (109)$$

The inequality of eq 95 also simplifies eq 76 as

$$E_g = \{K_{11}^+ - 2K_{12}^+ \mu_g\} / V \quad (110)$$

From eq 103, 109, and 110 with eq 99, one can derive the relation;

$$3(1 - 2\mu_g) = E_g \beta_g \quad (111)$$

This relation is well known for isotropic substances.

Under the approximation of eq 98, eq 90 is expressed as

$$C_{pg}^{\text{inter}} = T\alpha_g \sum_{k=1}^3 (\partial S_2^+ / \partial \ln I_k^+)_{T, i \neq k} / 3 + T(\partial S_2^+ / \partial T)_{i1,2,3} \quad (112)$$

Finally one can obtain the following relations at the glass transition from eq 101, 103, 105, 107', 87, and 112:

$$\beta_{1L}^+ = \beta_g \quad (113)$$

$$\alpha_{1L}^+ = \alpha_g \quad (114)$$

$$C_{p1L}^+ = C_{pg}^{\text{inter}} \quad (115)$$

Then, it follows from eq 88, 104, and 100 that

$$TV(\Delta\alpha)^2 / \Delta C_p^{\text{inter}} \Delta\beta = 1 \quad (116)$$

where

$$\Delta C_p^{\text{inter}} \equiv C_{p1L}^{\text{inter}} - C_{p1L}^+ = C_{p1L}^{\text{inter}} - C_{pg}^{\text{inter}} \quad (117)$$

$$\Delta\alpha \equiv \alpha_{1L} - \alpha_{1L}^+ = \alpha_{1L} - \alpha_g \quad (118)$$

$$\Delta\beta \equiv \beta_{1L} - \beta_{1L}^+ = \beta_{1L} - \beta_g \quad (119)$$

Similarly one has from eq 100, 103, 104, and 107' (or 101 and 105)

$$(\partial S_2^c / \partial \ln \tilde{V}) = V \Delta\alpha / \Delta\beta \quad (120)$$

$$\tilde{K} = V / \Delta\beta \quad (100')$$

$$(\partial K_2^+ / \partial T)_{i1,2,3} = (\partial S_2^+ / \partial \ln I_2^+)_{i \neq 2} = V\alpha_{1L}^+ / \beta_{1L}^+ = V\alpha_g / \beta_g \quad (121)$$

From eq 23, 27, 43, 77, 100, and 101, we have

$$(\partial \ln I_i^+ / \partial \ln V)_{T,L_1}^1 = (\partial \ln I_i^+ / \partial \ln V)_{T,P}^1 = \beta_{1L}^+ / 3\beta_{1L} \quad (122)$$

$$(\partial \ln \tilde{V} / \partial \ln I_i^+)_{T,L_1}^1 = (\partial \ln V / \partial \ln I_i^+)_{T,P}^1 = 3\Delta\beta / \beta_{1L}^+ \quad (123)$$

It is finally pointed out that in the present approximations the derivatives under constant length in the liquid state, α_{1L} , β_{1L} , and C_{p1L} , depend little on L_1 and become equal to those at $\sigma=0$. (APPENDIX II) Therefore, α_{p1L}^+ , β_{1L}^+ , and C_{p1L}^+ , accordingly α_g , β_g and C_{pg} because of eq 113—

115, are also regarded as independent of the length in the present treatment.

Expressions for Stretch Effect on Glass Transition Temperature

First, the configurational thermodynamic quantity S^c (or U^c) is defined as a part of S (or U) which is frozen-in in the glassy states: (cf. eq 10)

$$S^c = S_1^c(\lambda, b) + S_2^c(\tilde{V}) \quad (124)$$

$$U^c = U_1^c(\lambda, b) + U_2^c(\tilde{V}) \quad (125)$$

Putting $Y_s = T$, $Y_t = L_1$, and $X = S^c$ in eq 13, we have

$$(\partial T / \partial L_1)_g = \{ -(\partial S^c / \partial L_1)_{T,P}^1 + (\partial S^c / \partial L_1)_g \} / (\partial S^c / \partial T)_{L_1,P}^1 \quad (126)$$

The term $(\partial S^c / \partial L_1)_{T,P}^1$ is expressed with the aid of eq 92, 121, 122, and $(\partial P / \partial T)_{V,L_1}^1 \equiv \alpha_{1L} / \beta_{1L}$, as

$$\begin{aligned} (\partial S^c / \partial L_1)_{T,P}^1 &= (\partial S / \partial L_1)_{T,P}^1 - \{ (\partial S_2^+ / \partial L_1)_{T,P} + (\partial S_1^a / \partial L_1)_{T,P}^1 \} \\ &= (\partial S / \partial L_1)_{T,P}^1 + (\partial V / \partial L_1)_{T,P}^1 (\partial P / \partial T)_{V,L_1}^1 \\ &\quad - \{ (\partial S_2^+ / \partial \ln l_i^+)_{T,P} (\partial \ln l_i^+ / \partial \ln V)_{T,P}^1 \\ &\quad \times (\partial \ln V / \partial L_1)_{T,P}^1 \\ &\quad + (\partial S_1^a / \partial \ln a_i)_{T,P} (\partial \ln a_i / \partial L_1)_{T,P}^1 \} \end{aligned} \quad (127)$$

$$= -f_s / T + \Delta \alpha (\partial V / \partial L_1)_{T,P}^1 / \beta_{1L} \quad (128)$$

Here, f_s is derived as

$$\begin{aligned} f_s &\equiv T(\partial S / \partial L_1)_{T,P}^1 \\ &\equiv T(\partial S / \partial L_1)_{T,P}^1 + T(\partial P / \partial T)_{V,L_1}^1 (\partial V / \partial L_1)_{T,P}^1 \end{aligned} \quad (129)$$

On the other hand, $(\partial S^c / \partial T)_{L_1}^1$ is evaluated with eq 82, 85, 86, 87, and 92, as

$$\begin{aligned} (\partial S^c / \partial T)_{L_1}^1 &= C_{p1L}^{\text{inter}} - C_{p1L}^+ + C_{p1L}^{\text{intra}} - C_{pg}^{\text{intra}} \\ &= \Delta C_p^{\text{inter}} + \Delta C_p^{\text{intra}} \end{aligned} \quad (130)$$

$$\equiv \Delta C_p \quad (130')$$

Accordingly, from eq 126, 128, and 130', one has

$$\begin{aligned} (\partial T / \partial L_1)_g &= \{ f_s - T \Delta \alpha (\partial V / \partial L_1)_{T,P}^1 / \beta_{1L} \} / \Delta C_p \\ &\quad + (\partial S^c / \partial L_1)_g / \Delta C_p \end{aligned} \quad (131)$$

With the same process as the above derivation in the case of $X = S^c$, one can obtain the expression for $X = U^c$ as follows.

$$\begin{aligned} (\partial T / \partial L_1)_g &= \{ -(\partial U^c / \partial L_1)_{T,P}^1 \\ &\quad + (\partial U^c / \partial L_1)_g \} / (\partial U^c / \partial T)_{L_1,P}^1 \end{aligned} \quad (132)$$

$$(\partial U^c / \partial L_1)_{T,P}^1 = f_e + T \Delta \alpha (\partial V / \partial L_1)_{T,P}^1 / \beta_{1L} \quad (133)$$

$$(\partial U^c / \partial T)_{L_1,P}^1 = \Delta C_p \quad (134)$$

where

$$f_e \equiv (\partial U / \partial L_1)_{T,P}^1 \quad (135)$$

Then, substituting eq 133 and 134 into eq 132, one has

$$\begin{aligned} (\partial T / \partial L_1)_g &= \{ -f_e - T \Delta \alpha (\partial V / \partial L_1)_{T,P}^1 / \beta_{1L} \} / \Delta C_p \\ &\quad + (\partial U^c / \partial L_1)_g / \Delta C_p \end{aligned} \quad (136)$$

On the other hand, choosing the variables in eq 13 as $Y_s = T$, $Y_t = L_1$, and $X = \tilde{V}$, one has with the use of eq 117, 122, and 123,

$$\begin{aligned} (\partial T / \partial L_1)_g &= \{ -(\partial \ln \tilde{V} / \partial L_1)_{T,P}^1 \\ &\quad + (\partial \ln \tilde{V} / \partial L_1)_g \} / (\partial \ln \tilde{V} / \partial T)_{L_1,P}^1 \\ &= -(\Delta \beta / \Delta \alpha) (\partial \ln V / \partial L_1)_{T,P}^1 / \beta_{1L} \\ &\quad + (\partial \ln \tilde{V} / \partial L_1)_g / \Delta \alpha \end{aligned} \quad (137)$$

Specific Volume and Enthalpies of the Glasses Having Histories of Stretching

Differences in specific volume and enthalpy between two glasses having different histories of stretching compared at the state $(T, \sigma=0)$ are designated as

$$\Delta_g \ln V = \ln V(\text{Glass II}) - \ln V(\text{Glass I}) \quad (138)$$

$$\Delta_g H = H(\text{Glass II}) - H(\text{Glass I}) \quad (139)$$

Here, it is provided that the reference glass (Glass I) has been formed at the state $(T_{g0}, L_{10}, \sigma=0)$, and that Glass II has been formed at the state $(T_g, L_1, \sigma=\sigma_g)$. From eq 23 and 27, $\Delta_g \ln V$ is separated into two parts:

$$\Delta_g \ln V = \Delta_g \ln \tilde{V} + \Delta_g \ln V^+ \quad (140)$$

The first term $\Delta_g \ln \tilde{V}$ is given from eq 137 as

$$\Delta_g \ln \tilde{V} = (\Delta \beta / \beta_{1L}) (\Delta \ln V)^1 + \Delta \alpha \Delta T_g \quad (141)$$

since $\tilde{V}$ is invariable once the glass is formed, where $(\Delta \ln V)^1$ is the volume dilatation with stretching in the liquid state, i.e.,

$$\int_{L_{10}}^{L_1} (\partial \ln V / \partial L_1)_{T,P}^1 dL_1, \quad \text{and} \quad \Delta T_g = T_g - T_{g0}.$$

As described in the preceding section, the anisotropy in the liquid-like properties is disregarded here, the dependence of α_g on L_1 is also neglected. Hence, the second term $\Delta_g \ln V^+$ in eq 140 is expressed as

$$\Delta_g \ln V^+ = (\Delta \ln V^+)^1 + \int_{\sigma_g}^0 (\partial \ln V^+ / \partial \sigma)_{T,P}^g d\sigma \quad (142)$$

Since the integrand of the second term in eq 142 is evaluated from eq 111 as

$$\begin{aligned} (\partial \ln V^+ / \partial \sigma)_{P,T}^g d\sigma \\ = (\partial \ln V / \partial \sigma)_{P,T}^g d\sigma \\ = (\partial \ln V / \partial \ln L_1)_{P,T}^g (\partial \ln L_1 / \partial \sigma)_{P,T}^g d\sigma \\ = (1 - 2\mu_g) E_g^{-1} d\sigma = \beta_g d\sigma / 3, \end{aligned}$$

we have

$$\Delta_g \ln V^+ = (\beta_g / \beta_{1L}) (\Delta \ln V)^1 - \beta_g \sigma_g / 3 \quad (143)$$

Accordingly, one obtains from eq 140, 141, and 143

$$\Delta_g \ln V = \Delta \alpha \Delta T_g + (\Delta \ln V)^1 - \beta_g \sigma_g / 3 \quad (144)$$

On the other hand, with the aid of eq 33 and 124, the enthalpy difference $\Delta_g H$ is expressed as follows under the approximations of eq 95 and 94, and disregarding the anisotropy in the liquid-like properties:

$$\begin{aligned} \partial \Delta_g H / \partial L_1 &= (\partial \Delta_g U^c / \partial L_1) + (\partial \Delta_g U_1^a / \partial L_1) \\ &\quad + (\partial \Delta_g U_2^+ / \partial L_1) + P(\partial \Delta_g V / \partial L_1) \\ &\cong (\partial U^c / \partial L_1)_g + (\partial U_2^+ / \partial \ln L_2^+)_{i \neq 2} \\ &\quad \times (\partial \Delta_g \ln V^+ / \partial L_1) \end{aligned} \quad (145)$$

Since $(\partial U_2^+ / \partial \ln L_2^+)_{i \neq 2} \cong T(\partial S_2^+ / \partial \ln L_2^+)_{i \neq 2}$ because of eq 29 with eq 95, eq 145 reduces by the use of eq 136, 121, and 143, to

$$\begin{aligned} \partial \Delta_g H / \partial L_1 &= f_e + \Delta C_p (\partial T / \partial L_1)_g + (TV \alpha_{1L} / \beta_{1L}) \\ &\quad \times (\partial \ln V / \partial L_1)_{T,P}^1 - TV \alpha_g (\partial \sigma_g / \partial L_1) / 3 \end{aligned} \quad (146)$$

Replacing $(\partial \ln V / \partial L_1)_{T,P}^1$ in eq 146 by $(\partial \Delta_g \ln V / \partial L_1)$ with eq 144, one obtains an alternative form

$$\begin{aligned} \partial \Delta_g H / \partial L_1 \\ = f_e + (\Delta C_p - TV \Delta \alpha_{1L} / \beta_{1L}) (\partial T / \partial L_1)_g \\ + (TV \alpha_{1L} / \beta_{1L}) (\partial \Delta_g \ln V / \partial L_1) \\ + TV (\beta_g \alpha_{1L} / \beta_{1L} - \alpha_g) (\partial \sigma_g / \partial L_1) / 3 \end{aligned} \quad (147)$$

Criteria for the Glass Transition and Thermodynamic Equations

The three criteria for the glass transition are here considered as in a previous paper¹:

$$(1) \text{ iso-hole fraction or iso-free volume (iso-} V_f) \quad (d\tilde{V})_g = 0 \quad (148)$$

$$(2) \text{ iso-configurational entropy (iso-} S^c) \quad (dS^c)_g = 0 \quad (149)$$

$$(3) \text{ iso-configurational energy (iso-} U^c) \quad (dU^c)_g = 0 \quad (150)$$

The combination of eq 137, 131, and 136 with eq 148, 149, and 150 give the expressions for $(\partial T / \partial L_1)_g$ for each criterion:

For iso- V_f ;

$$(\partial T / \partial L_1)_g = -(\Delta \beta / \Delta \alpha) (\partial \ln V / \partial L_1)_{T,P}^1 / \beta_{1L} \quad (151)$$

For iso- S^c ;

$$\begin{aligned} (\partial T / \partial L_1)_g &= \{T(\partial f / \partial T)_{P,L}^1 \\ &\quad + TV \alpha_g (\partial \ln V / \partial L_1)_{T,P}^1\} / \Delta C_p \end{aligned} \quad (152)$$

$$= \{f_s - T \Delta \alpha (\partial V / \partial L_1)_{T,P}^1 / \beta_{1L}\} / \Delta C_p \quad (152')$$

For iso- U^c ;

$$\begin{aligned} (\partial T / \partial L_1)_g &= \{f - T(\partial f / \partial T)_{P,L}^1 \\ &\quad + TV \alpha_g (\partial \ln V / \partial L_1)_{T,P}^1\} / \Delta C_p \end{aligned} \quad (153)$$

$$= \{-f_e - T \Delta \alpha (\partial V / \partial L_1)_{T,P}^1 / \beta_{1L}\} / \Delta C_p \quad (153')$$

With these formulas of $(\partial T / \partial L_1)_g$, the expressions of specific volume and enthalpy of the stretched glass for each criterion may be obtained from eq 144 and 146 or 147.

Application of Statistical Theory of Rubber Elasticity

One can apply the statistical theory of rubber elasticity to the present theory without any inconsistency. The results of the statistical theory required here are, with the use of Flory's expression,³

$$f = G(V_i / V_0)^{2/3} L_i^{-1} (\lambda - \lambda^{-2}) \quad (154)$$

$$f_e / f = 1 - f_s / f = d \ln \langle r^2 \rangle_0 / d \ln T \quad (155)$$

$$(\partial \ln V / \partial L_1)_{T,P} = \beta_{1L} G V_i^{-1/3} V_0^{-2/3} \lambda^{-2} L_i^{-1} \quad (156)$$

where $G = \nu k T$ (ν , number of effective network chains), V_i and L_i are the volume and length L_1 in the unstretched liquid state, i.e., at $\epsilon = \epsilon^*$; V_0 is the volume when $\epsilon = \epsilon_0$ or $\gamma = \mathbf{E}$ ($\mathbf{E}$, unit tensor); $\langle r^2 \rangle_0$ is unperturbed mean square end-to-end distance of a network chain corresponding to ϵ_0^2 ; and λ is L_1 / L_i equal to λ_1 defined in eq 28 and 29 under the condition of eq 94. The shear modulus G' is then $G' = G(V_i / V_0)^{2/3} / V$. Substituting eq 154—156 to eq 144 and 146, we obtain, noticing $\sigma = f L_1 / V$,

$$\Delta_g \ln V = \Delta \alpha \Delta T_g + G' \{\beta_{1L} (1 - \lambda^{-1}) - \beta_g (\lambda^2 - \lambda^{-1}) / 3\} \quad (157)$$

$$\begin{aligned} \Delta_g H &= G' V (d \ln \langle r^2 \rangle_0 / d \ln T) \\ &\quad \times (\lambda^2 / 2 + \lambda^{-1} - 3/2) + TV \alpha_{1L} G' (1 - \lambda^{-1}) \\ &\quad - TV \alpha_g G' (\lambda^2 - \lambda^{-1}) / 3 + \Delta C_p \Delta T_g \end{aligned} \quad (158)$$

On the other hand, from eq 151–153 with eq 154–156, one has the expressions for the change in glass transition temperature for each criterion:

For iso- V_f ;

$$\Delta T_g = -(\Delta\beta/\Delta\alpha)G'(1-\lambda^{-1}) \quad (159)$$

For iso- S^c ;

$$\Delta T_g = (G'V/\Delta C_p)(1 - d \ln \langle r^2 \rangle_0 / d \ln T) \times (\lambda^2/2 + \lambda^{-1} - 3/2) - (G'TV\Delta\alpha/\Delta C_p)(1 - \lambda^{-1}) \quad (161)$$

For iso- U^c

$$\Delta T_g = -(G'V/\Delta C_p)(d \ln \langle r^2 \rangle_0 / d \ln T) \times (\lambda^2/2 + \lambda^{-1} - 3/2) - (G'TV\Delta\alpha/\Delta C_p)(1 - \lambda^{-1}) \quad (161)$$

Substituting these formulas of ΔT_g into eq 157 and 158, one can derive the expressions of $\Delta_g \ln V$ and $\Delta_g H$ of the stretched glass for each criterion.

DISCUSSION

Criteria for Glass Transition

With the aid of eq 151–153 or 159–161, the three criteria for the glass transition may be checked by the measurements of the change in T_g with stretching, $\partial T_g / \partial L_1 [= (\partial T / \partial L_1)_g]$. According to the iso-free volume assumption, *i.e.*, eq 151, T_g decreases with stretching since the number of holes, accordingly the free volume, increases with elongation because the volume dilatation is induced by stretching, *i.e.*, $(\partial \ln V / \partial L_1)_{T,P}^1 > 0$. On the other hand, if the iso- S^c assumption is valid, T_g should increase by stretching as seen from eq 152 because $(\partial f / \partial T)_{P,L_1}^1$ may be positive in network polymers. In the third case expressed by eq 153, the change in T_g may be small, since $f - T(\partial f / \partial T)_{P,L_1}^1$ may be smaller than f and the volume dilatation is also small. The term f_s (or $-f_s$) in eq 152' (or 153') indicates the contribution of the decrease in S^c (or U^c) arising from the decrease in conformational entropy (or energy) of network chains with stretching, and the second term in the braces { } in eq 152' (or 153') indicates the contribution of the increase in S^c (or U^c) arising from the increase in the free volume, in other words the number of holes, with stretching.

It has been suggested from the free volume theory that the relaxation time for microbrownian

motion reduces with stretching. This leads to the prediction that T_g decreases by stretching: The fractional free volume f is expressed as a function of temperature and strain ϵ , according to Ferry and Stratton,⁴ by

$$f = f_{g0} + \alpha_f(T - T_{g0}) + (\beta_f/\beta)(1 - 2\mu)\epsilon \quad (162)$$

where T_{g0} is T_g at $\epsilon=0$, f_{g0} is f at $T=T_g$ and $\epsilon=0$, and α_f and β_f are the thermal expansion coefficient and compressibility of free volume respectively. If the free volume at T_g is kept constant, one has from eq 162

$$T_g - T_{g0} = -(\beta_f/\beta)(1 - 2\mu)\epsilon/\alpha_f \quad (163)$$

If $\beta_f = \Delta\beta$ and $\alpha_f = \Delta\alpha$ are assumed, eq 163 is identical to eq 151, when strain is small, since $(\partial \ln V / \partial \ln L_1)_{T,P}^1 = 1 - 2\mu_1$, and $(L_1 - L_{10})/L_1 = \epsilon$.

On the other hand, Gee, *et al.*,⁵ studied thermodynamically the T_g of stretched network polymers by introducing one ordering parameter z , and derived the expression for $\partial T_g / \partial L_1$ based on the assumption that z is constant at T_g . The result obtained is

$$\partial T_g / \partial L_1 = (T/\Delta C_p) \Delta(\partial f / \partial T)_{P,L_1} \quad (164)$$

They made the approximation $T\Delta(\partial f / \partial T)_{P,L_1} \cong T(\partial f / \partial T)_{P,L_1}^1 \cong f$ in comparing with experiments.* Namely, they presented

$$T_g - T_{g0} = \frac{T_{g0}}{\Delta C_p T_0} \int_{L_{10}}^{L_1} f dL_1 \quad (165)$$

The term $\int_{L_{10}}^{L_1} f dL_1$ represents the work of stretching at T_0 .

Equation 164 with $T\Delta(\partial f / \partial T)_{P,L_1} = T(\partial f / \partial T)_{P,L_1}^1$ is equivalent to eq 152 for iso- S^c in the present theory if the second term in eq 152 arising from the volume dilatation with stretching is ignored.

* The author does not agree with their approximation because no evidence is found for $(\partial f / \partial T)_{P,L_1}^2 \ll (\partial f / \partial T)_{P,L_1}^1$. The fact that the term $(\partial f / \partial T)_{P,L_1}^1$ appears in the present theory instead of $\Delta(\partial f / \partial T)_{P,L_1}^1$ in eq 164 arises from the inequality between $(dZ^c)^1$ and $\Delta(dZ)$ as expressed by eq 12. For example, $\Delta(\partial a_i / \partial L_1)_{P,T} \neq 0$ and $\Delta(\partial l_i^+ / \partial L_1)_{P,T} \neq 0$. On the other hand, the change in the cell volume with temperature and pressure can be approximated to be the same both in the liquid and glassy states under low pressure if the free energy is expressed by eq 10.¹ This leads to eq 14 and 15.

DiMarzio⁶ also evaluated the change in T_g with stretching based on the assumption of iso- S^c at T_g and the ideal rubber elasticity. The result obtained is identical to eq 160 when $f_0/f = d \ln \langle r^2 \rangle_0 / d \ln T = 0$ and, if the second term indicating the effect of the volume expansion is disregarded: *i.e.*,

$$\Delta T_g = (G'V/\Delta C_p)(\lambda^2/2 + \lambda^{-1} - 3/2) \quad (166)$$

The experimental facts show that the sign of $(\partial T_g / \partial L_1)$ depends on the method of measurement of T_g .⁷ However, the glass transition temperature defined as the temperature at which the micro-brownian motion is frozen-in, as discussed in previous papers, may correspond to T_g observed by the volume-temperature measurement under cooling at constant length.* Such measurements were made by Gee, *et al.*⁵ According to their experiments, T_g increases with stretching approximately by the amount predicted from their equation, eq 165. With the aid of their data, DiMarzio concluded from his theory, eq 166, that the iso- S^c assumption for T_g is valid. The result of the present theory also suggests that the iso- S^c , not the iso- V_f and the iso- U^c , is a valid criterion for T_g , because the second term of eq 152' and f_0 may be small compared with f . The measurement of T_g under elevated pressure cannot distinguish between the two criteria, the iso- S^c and the iso- U^c , as described in a preceding paper.¹ The examination of $(\partial T_g / \partial L_1)$, however, makes it possible.

In order to test the criteria for T_g in more detail, the T_g-L_1 relation (from $T-V$ curve under constant L_1), α , β , C_p , and f for a styrene-butadiene copolymer (butadiene content = 10 wt%) were measured and compared with eq 159–161.⁸ As the result, it was found that the experiment supports the iso- S^c assumption for T_g .

Inserting eq 151–153 into eq 144 and 146, one has the expressions of $\Delta_g \ln V$ and $\Delta_g H$ for each criterion, by which one may also test the criteria with the measurements of specific volume and

enthalpy of a stretched glass.

Enthalpy of Stretched Glass

According to eq 147, the enthalpy of stretched glass depends not only on the conformational energy of stretched network chains expressed by $\int_{L_{10}}^{L_1} f_0 dL_1$, but also on the freezing temperature, T_g , and the specific volume of the glass. Stölting and Müller⁹ obtained the enthalpy difference $\Delta_g H$ of stretched polystyrene glass by measurement of the heat of solution, and concluded that $\Delta_g H$ for the glass stretched above 124°C is explained by the change in the energy arising from the variation in chain conformation with stretching. The author, however, believes that in general $\Delta_g H$ is controlled not only by the change in the conformation with stretching, but also by the glass-forming temperature and the specific volume of the glass, which are also the factors determining the energies associated with chain conformation and intersegmental interactions.

Finally it can be noted that eq 147 gives the method of evaluating the energetic elasticity f_0 from the measurements of $\Delta_g H$, $\Delta_g \ln V$, α_g , and T_g .

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APPENDIX I

From the equations of state, the quantities defined by eq 50–61 can be expressed in terms of various K defined by eq 39–42 and 62–65.

Differentiating eq 45 with temperature under constant pressure gives

$$\begin{aligned} & -V\alpha_{1L}P \\ & = (\partial K_2^{\lambda} / \partial T)_{P, L_1}^1 + (\partial K_2^+ / \partial T)_{P, L_1}^1 \\ & = (\partial K_2^{\lambda} / \partial T)_{P, L_1}^1 + \tilde{K}(\partial \ln \tilde{V} / \partial T)_{P, L_1}^1 - (\partial S_2^c / \partial \ln \tilde{V}) \\ & = (\partial K_2^{\lambda} / \partial T)_{P, L_1}^1 + \tilde{K}(\alpha_{1L} - \alpha_{1L}^+) - (\partial S_2^c / \partial \ln \tilde{V}) \end{aligned} \quad (A-1)$$

From eq 33 and 37, one has

$$\begin{aligned} & \sum_{k=1}^3 K_{2k}^+ (\partial \ln I_k^+ / \partial T)_{P, L_1}^1 + (\partial K_2^+ / \partial T)_{P, L_1}^1 \\ & = \tilde{K}(\partial \ln \tilde{V} / \partial T)_{P, L_1}^1 - (\partial S_2^c / \partial \ln \tilde{V}) \end{aligned} \quad (A-2)$$

With the aid of eq 27 and 43, eq A-2 becomes

* The glass transition temperature should depend on the cooling rate. For the sake of testing the criteria for T_g , therefore, data using the same cooling rate must be used. T_g in the expressions of $\Delta_g H$ and $\Delta_g \ln V$ is not necessarily that of the same cooling rate, however, and implies only the glass-forming temperature.

$$\alpha_{1L}^+ \sum_{k=1}^3 K_{2k}^+/3 + (\partial K_2^+/\partial T)_{1,2,3}^+ \\ = \tilde{K}(\alpha_{1L} - \alpha_{1L}^+) - (\partial S_2^c/\partial \ln \tilde{V}) \quad (A-3)$$

Then, from eq A-1 and A-3 one has eq 66 and 67;

$$\alpha_{1L}^+ = 3\{(\partial K_2^+/\partial T)_{1,2,3}^+ + (\partial K_2^{\lambda}/\partial T)_{P,L_1}^+ \\ + PV\alpha_{1L}\}/\sum_{k=1}^3 K_{2k}^+ \quad (67)$$

or

$$\alpha_{1L} - \alpha_{1L}^+ = \{(\partial S_2^c/\partial \ln \tilde{V}) - (\partial K_2^{\lambda}/\partial T)_{P,L_1}^+ \\ - VP\alpha_{1L}\}/\tilde{K} \quad (66)$$

On the other hand, thermal expansion coefficient

α_{gL} of the glassy state is derived from eq 48. Differentiating eq 48 with temperature under constant pressure and constant length, one has

$$-V\alpha_{gL}P \\ = (\partial K_2^a/\partial T)_{P,L_1}^g + (\partial K_2^+/ \partial T)_{P,L_1}^g \\ = \sum_{k=1}^3 K_{2k}^g (\partial \ln a_k/\partial T)_{P,L_1}^g + (\partial K_2^a/\partial T)_{a_{1,2,3}} \\ + \sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+/\partial T)_{P,L_1}^g + (\partial K_2^+/\partial T)_{1,2,3}^+ \quad (A-4)$$

Since $(\partial \ln a_k/\partial T)_{P,L_1}^g = (\partial \ln l_k^+/\partial T)_{P,L_1}^g = \alpha_{gL}/2$ for $k=2$ and 3 , and $(\partial \ln a_1/\partial T)_{P,L_1}^g = (\partial \ln l_1^+/\partial T)_{P,L_1}^g = 0$, eq A-4 reduces to eq 68;

$$\alpha_{gL} = -\{(\partial K_2^+/\partial T)_{1,2,3}^+ + (\partial K_2^a/\partial T)_{a_{1,2,3}}\} \\ \{ \sum_{k=2}^3 K_{2k}^+/2 + \sum_{k=2}^3 K_{2k}^g/2 + PV \} \quad (68)$$

Similarly, eq 69 for α_g is derived.

The isothermal compressibility β_{1L} at constant length in the liquid state is derived from eq 45 as

$$\beta_{1L}^{-1} \equiv -(\partial P/\partial \ln V)_{T,L_1}^1 = P + [\partial(K_2^{\lambda} + K_2^+)/\partial V]_{T,L_1}^1 \quad (A-5)$$

$$= P + \sum_{k=1}^3 K_{2k}^{\lambda} (\partial \ln \lambda_k/\partial V)_{T,L_1}^1 + \tilde{K}(\partial \ln \tilde{V}/\partial V)_{T,L_1}^1 \\ = P + P^{\lambda} + \tilde{K}V^{-1}\{1 - (\partial \ln V^+/\partial \ln V)_{T,L_1}^1\} \\ = P + P^{\lambda} + \tilde{K}(1 - \beta_{1L}^+/\beta_{1L})/V \quad (A-6)$$

where P^{λ} is defined by eq 78. Total differentials of K_2^+ and $\tilde{K}$ are written, from the definition of eq 39 and 40 with the aid of eq 33, as

$$dK_2^+ = \sum_{k=1}^3 K_{2k} d \ln l_k^+ + (\partial S_2^+/\partial \ln l_2^+)_{T,L_1} dT \quad (A-7)$$

$$d\tilde{K} = \tilde{K} d \ln \tilde{V} + (\partial S_2^c/\partial \ln \tilde{V}) dT \quad (A-8)$$

Then from eq 45, A-7 and A-8, one has

$$\sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+/\partial \ln P)_{T,L_1}^1 = \tilde{K}(\partial \ln \tilde{V}/\partial \ln P)_{T,L_1}^1 \quad (A-9)$$

Since eq 43 holds in the liquid state, eq A-9 reduces to

$$\beta_{1L}^+ \sum_{k=1}^3 K_{2k}^+/3 = \tilde{K}(\beta_{1L} - \beta_{1L}^+) \quad (A-10)$$

Accordingly, eq A-6 and A-10 yield eq 70 and 71:

$$\beta_{1L}^+ = 3V\{1 - (P + P^{\lambda})\beta_{1L}\}/\sum_{k=1}^3 K_{2k}^+ \quad (71)$$

$$\beta_{1L} - \beta_{1L}^+ = V\{1 - (P + P^{\lambda})\beta_{1L}\}/\tilde{K} \quad (70)$$

On the other hand β_{gL} is expressed from eq 48 as

$$\beta_{gL}^{-1} = P + \sum_{k=1}^3 K_{2k}^g (\partial \ln a_k/\partial V)_{T,L_1}^g \\ + \sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+/\partial V)_{T,L_1}^g \\ = P + P^a + \sum_{k=2}^3 K_{2k}^+/2V \quad (72)$$

where

$$P^a = \sum_{k=1}^3 K_{2k}^g (\partial \ln a_k/\partial V)_{T,L_1}^g = \sum_{k=2}^3 K_{2k}^g/2V \quad (79)$$

and $(d \ln l_1^+)_{L_1}^g = (d \ln a_1)_{L_1}^g = 0$ was used. Similarly, eq 70 for β_g is derived.

Next, $(\partial \ln V/\partial \ln L_1)_{T,P}^1 = 1 - 2\mu_1$ is evaluated. From eq 45

$$-VP(\partial \ln V/\partial L_1)_{T,P}^1 \\ = (\partial K_2^{\lambda}/\partial L_1)_{T,P}^1 + \sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+/\partial L_1)_{T,P}^1 \quad (A-12)$$

On the other hand, from eq 37 with eq A-7 and A-8, one has

$$\sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+/\partial L_1)_{T,P}^1 = \tilde{K}(\partial \ln V/\partial L_1)_{T,P}^1 \quad (77)$$

Using the relation $(\partial \ln V/\partial L_1)_{T,P}^1 = (\partial \ln \tilde{V}/\partial L_1)_{T,P}^1 + 3(\partial \ln l_k^+/\partial L_1)_{T,P}^1$ derived from eq 23 and 43, one obtains with eq A-12 and 77,

$$(\partial \ln V/\partial \ln L_1)_{T,P}^1 \\ = - \frac{(\partial K_2^{\lambda}/\partial \ln L_1)_{T,P}^1 (3\tilde{K} + \sum_{k=1}^3 K_{2k}^+)}{\tilde{K} \sum_{k=1}^3 K_{2k}^+ + PV(3\tilde{K} + \sum_{k=1}^3 K_{2k}^+)} \quad (74)$$

In the glassy state, eq 48 yields

$$-VP(\partial \ln V/\partial \ln L_1)_{T,P}^g$$

$$= \sum_{k=1}^3 K_{2k}^a (\partial \ln a_k / \partial \ln L_1)_{T,P}^g + \sum_{k=1}^3 K_{2k}^+ (\partial \ln l_k^+ / \partial \ln L_1)_{T,P}^g \quad (\text{A-13})$$

Since

$$(\partial \ln a_1 / \partial \ln L_1)_{T,P}^g = (\partial \ln l_1^+ / \partial \ln L_1)_{T,P}^g = 1 \quad (\text{A-14})$$

and

$$(\partial \ln a_k / \partial \ln L_1)_{T,P}^g = (\partial \ln l_k^+ / \partial \ln L_1)_{T,P}^g = \{(\partial \ln V / \partial \ln L_1)_{T,P}^g - 1\} / 2 \quad (\text{A-15})$$

for $k=2$ and 3 , then eq 75 can be derived as

$$\begin{aligned} & (\partial \ln V / \partial \ln L_1)_{T,P}^g \\ &= \left\{ \sum_{k=2}^3 K_{2k}^+ / 2 + P^a V - (K_{21}^a + K_{21}^+) \right\} / \\ & \quad \left\{ \sum_{k=2}^3 K_{2k}^+ / 2 + P^a V + PV \right\} \quad (\text{A-16}) \\ &= 1 - (K_{21}^a + K_{21}^+ + PV) / \left(\sum_{k=2}^3 K_{2k}^+ / 2 + P^a V + PV \right) \quad (75) \end{aligned}$$

Young's modulus $E_g = (\partial \sigma / \partial \ln L_1)_{T,P}^g$ in the glassy state is obtained by differentiating eq 44 with the length L_1 under $T, P = \text{constant}$:

$$\begin{aligned} & (\sigma - P)(\partial V / \partial \ln L_1)_{T,P}^g + V E_g \\ &= \sum_{k=1}^3 K_{1k}^a (\partial \ln a_k / \partial \ln L_1)_{T,P}^g \\ & \quad + \sum_{k=1}^3 K_{1k}^+ (\partial \ln l_k^+ / \partial \ln L_1)_{T,P}^g \quad (\text{A-17}) \end{aligned}$$

With the use of eq A-14 and A-15, eq A-17 reduces to eq 76;

$$E_g = \{K_{11}^a + K_{11}^+ - 2(K_{12}^a + K_{12}^+) \mu_g\} / V - (1 - 2\mu_g)(\sigma - P) \quad (76)$$

APPENDIX II

Since in the liquid state the total differential of $\ln V$ is written as

$$\begin{aligned} d \ln V = & (\partial \ln V / \partial L_1)_{T,P}^1 dL_1 + (\partial \ln V / \partial T)_{P,L_1}^1 dT \\ & + (\partial \ln V / \partial P)_{T,L_1}^1 dP \quad (\text{A-18}) \end{aligned}$$

one has

$$\begin{aligned} \alpha_1 \equiv & (\partial \ln V / \partial T)_{P,\sigma=0}^1 \\ = & (\partial \ln V / \partial L_1)_{T,P}^1 |_{\sigma=0} (\partial L_1 / \partial T)_{P,\sigma=0}^1 \\ & + (\partial \ln V / \partial T)_{P,L_1}^1 |_{\sigma=0} \quad (\text{A-19}) \end{aligned}$$

The symbol $|_{\sigma=0}$ indicates the value at $\sigma=0$. From the well known relation $1 - 2\mu = E\beta/3$ for isotropic

substances, $(\partial \ln V / \partial L_1)_{T,P}^1 |_{\sigma=0}$ is $E\beta/3$, and $3(\partial \ln L_1 / \partial T)_{P,\sigma=0}^1 = \alpha_1$, because of isotropy. One has then from eq A-19

$$\alpha_1(1 + E_1\beta_1/9) = \alpha_{1L} |_{\sigma=0} \quad (\text{A-20})$$

Under the condition of eq 95, $E_1\beta_1 \ll 1$. Accordingly, it follows from eq A-20 that

$$\alpha_1 = \alpha_{1L} |_{\sigma=0} \quad (\text{A-21})$$

On the other hand, one can expand α_{1L} at $\sigma=0$ as

$$\begin{aligned} \alpha_{1L} = & \alpha_{1L} |_{\sigma=0} + (\partial^2 \ln V / \partial \ln L_1 \partial T)_{P,\sigma=0}^1 \\ & \times \ln (L_1/L_{10}) + \dots \quad (\text{A-22}) \end{aligned}$$

where L_{10} is the length L_1 at $\sigma=0$. Since $(\partial \ln V / \partial \ln L_1)_{P,T}^1 |_{\sigma=0} = E_1\beta_1/3$ and $[\partial(E_1\beta_1)/\partial T]_{P,L_1} = O(E_1\beta_1/T)$, then from eq A-22

$$\alpha_{1L} = \alpha_{1L} |_{\sigma=0} + O(\beta_1\sigma/T) = \alpha_{1L} |_{\sigma=0} [1 + O(\sigma/P_1)] \quad (\text{A-23})$$

Under the condition of eq 96 (*i.e.*, $\sigma \ll P_1$) with eq A-21, eq A-23 reduces to

$$\alpha_{1L} = \alpha_{1L} |_{\sigma=0} = \alpha_1 \quad (\text{A-24})$$

Similarly to eq A-21, one has under eq 95

$$\beta_1 \equiv -(\partial \ln V / \partial P)_{T,\sigma=0}^1 = \beta_{1L} |_{\sigma=0} \quad (\text{A-25})$$

Corresponding to eq A-22, one has for β_{1L}

$$\begin{aligned} \beta_{1L} = & \beta_{1L} |_{\sigma=0} + (\partial^2 \ln V / \partial \ln L_1 \partial P)_{T,\sigma=0}^1 \\ & \times \ln (L_1/L_{10}) + \dots \quad (\text{A-26}) \end{aligned}$$

As seen from eq 100 and 101 with eq 121 and 122, β_{1L} depends on volume and temperature alone in the present approximations. Hence it follows that

$$\begin{aligned} & (\partial^2 \ln V / \partial \ln L_1 \partial P)_{T,\sigma=0}^1 \\ = & -(\partial \beta_{1L} / \partial \ln V)_{T,L_1}^1 (\partial \ln V / \partial \ln L_1)_{P,T}^1 |_{\sigma=0} \quad (\text{A-27}) \end{aligned}$$

Then, from eq A-25, A-26 and A-27, one has

$$\begin{aligned} \beta_{1L} = & \beta_{1L} |_{\sigma=0} + (\partial \ln \beta_1 / \partial P)_{T,\sigma=0}^1 \\ & \times (E_1\beta_1/3) \ln (L_1/L_{10}) + \dots \\ = & \beta_{1L} |_{\sigma=0} + \beta_1 O[\sigma(\partial \ln \beta_1 / \partial P)_{T,\sigma=0}] \quad (\text{A-28}) \end{aligned}$$

For liquids one can except $\sigma(\partial \ln \beta_1 / \partial P)_{T,\sigma=0} = O(10\sigma\beta) \ll 1$, as estimated from Tait's equation,¹⁰ $1 - (V/V_0) = C \ln(1 + P/B)$, which reproduces the experimental V - P relation under constant T very well, because the relation $(\partial \ln \beta / \partial P)_T = (V/V_0) \times \{(V/V_0)C + 1\} \beta \approx (1/C + 1)\beta \approx \beta/C$ is obtained from Tait's equation where V_0 is V at $P=0$, C

is a constant, about 0.1, and B is a function of T alone. Accordingly, one has finally from eq A-25 and A-28

$$\beta_{1L} = \beta_{1L}|_{\sigma=0} = \beta_1 \quad (\text{A-29})$$

As for heat capacity,

$$\begin{aligned} C_{p1} &\equiv T(\partial S/\partial T)_{P, \sigma=0}^1 \\ &= T(\partial S/\partial \ln L_1)_{T, P}^1 (\partial \ln L_1/\partial T)_{P, \sigma=0}^1 + C_{p1L}|_{\sigma=0} \end{aligned} \quad (\text{A-30})$$

Since one may expect $T(\partial S/\partial \ln L_1)_{T, P}^1 = O(fL_1)$ and $C_{p1} = O(TV\alpha_1^2/\beta_1)$, the first term of eq A-30 is estimated as

$$\begin{aligned} &T(\partial S/\partial \ln L_1)_{T, P}^1 (\partial \ln L_1/\partial T)_{P, \sigma=0}^1 \\ &= O(fL_1)\alpha_1/3 \\ &= C_{p1}O(fL_1\alpha_1\beta_1/TV\alpha_1^2) \\ &= C_{p1}O(\sigma/P_1) \end{aligned} \quad (\text{A-31})$$

Then, under the condition of eq 96, it follows from eq A-30 and A-31 that

$$C_{p1} = C_{p1L}|_{\sigma=0} \quad (\text{A-32})$$

Just the same as eq A-22,

$$C_{p1L} = C_{p1L}|_{\sigma=0} + T(\partial^2 S/\partial \ln L_1 \partial T)_{P, \sigma=0}^1 \ln(L_1/L_{10}) + \dots \quad (\text{A-33})$$

Since one may put $T(\partial S/\partial \ln L_1)_{T, P}^1 = O(fL_1)$ again and $(\partial f/\partial T)_{P, L_1} = O(f/T)$, the second term of eq A-33 is evaluated as

$$\begin{aligned} &T(\partial S/\partial \ln L_1 \partial T)_{P, \sigma=0}^1 = O(fL_1/T) \ln(L_1/L_{10}) \\ &= O[f(L_1 - L_{10})/T] \end{aligned} \quad (\text{A-34})$$

Then, with the same consideration as in the evaluation of eq A-31, one has, from eq A-32 ~ A-34 under the condition of $\sigma/(P_1/\alpha T) \ll 1$,

$$C_{p1L} = C_{p1L}|_{\sigma=0} = C_{p1} \quad (\text{A-35})$$

With the same arguments as the above, one may show that the dependence of α_{1L}^+ , β_{1L}^+ , and C_{p1L}^+ on the length L_1 can be ignored under the conditions of eq 95 and 96.

As far as the form of free energy of eq 33, where F_2 representing the liquidlike properties is not a function of λ and a but a function of volume and temperature alone in the liquid state, the dependence of α_{1L} , β_{1L} , and C_{p1L} on the length can be ignored from the fact that the Young's modulus is sufficiently lower than the bulk modulus and the internal pressure in the liquid state.

REFERENCES

1. T. Nose, *Polymer J.*, **2**, 445 (1971).
2. J. Meixner, *Kolloid-Z.*, **134**, 3 (1953); R. O. Davies and G. O. Jones, *Proc. Roy. Soc.*, **A-217**, 26 (1953), *Advances in Physics*, **2**, 370 (1953).
3. P. J. Flory, *Trans. Faraday Soc.*, **67**, 829 (1961).
4. J. D. Ferry and R. A. Stratton, *Kolloid-Z.*, **171**, 107 (1960).
5. G. Gee, P. N. Hartley, T. B. M. Herbert, and H. A. Lanceley, *Polymer*, **1**, 365 (1960).
6. E. A. DiMarzio, *J. Res. Nat. Bur. Std.*, **68A**, 611 (1964).
7. T. Nose, *J. Soc. Rubber Ind., Japan*, **44**, 961 (1971).
8. A. Komatsu and T. Nose, *Rept. Progr. Polym. Phys. Japan*, **14**, 309 (1971).
9. J. Stölting and F. H. Müller, *Kolloid-Z. Polym.*, **238**, 459 (1970); *ibid.*, **240**, 792 (1970).
10. W. G. Cutler, H. McMicklo, W. Weff, and R. W. Sciessler, *J. Chem. Phys.*, **29**, 272 (1958); V. S. Nanda and R. Simha, *J. Chem. Phys.*, **41**, 1884, 3870 (1964); J. Becht, K. H. Hellwege, and W. Knappe, *Kolloid-Z.*, **216**—**217**, 150 (1967); H. Breuer and G. Rehage, *ibid.*, **216**—**217**, 159 (1967).